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Detection of an Intermediate in the Oxygenation of Triphenylphosphine to Triphenylphosphine Oxide by [(trpy)(bpy)Ru(O)]²⁺
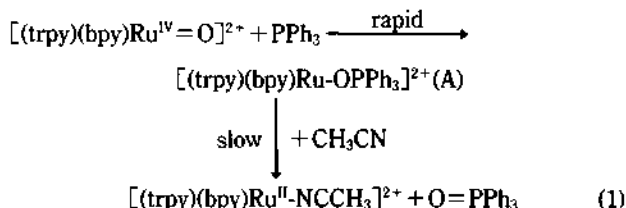
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The search for metal complexes capable of performing regio- and stereospecific oxidations is an important area of work in oxidative catalysis and hydrocarbon oxidation reactions. A family of oxo reagents such as $Cr_2O_7^{-2}$ or MnO_4^- are of obvious value as catalysts, though their reactions are difficult to control because of their multi-oxo site.[1] Recently, the cleavage of DNA by the metal-oxo complexes has been also studied.[2]

The development of metal mono-oxo complexes with systematic variations in the ligand environment could lead to the control of the redox potential[3] We reported a series of stoichiometric and catalytic oxidations of inorganic and organic substrates by high-valent oxidation state complexes of ruthenium mono-oxo complexes.[4]

Here we describe the spectroscopic properties of the Ru(II) intermediate complex, [(trpy)(bpy)Ru-OPPh₃]²⁺, in the rapid oxidation of PPh₃ by [(trpy)(bpy)Ru(O)]²⁺ (trpy is 2,2′ : 6′,2″-terpyridine and bpy is 2,2′-bipyridine.) in CH₃CN. The course of oxo group transfer from [(trpy)(bpy)Ru^{IV}=O]²⁺ to PPh₃ proceeds as shown in Eq. (1).

$$[(trpy)(bpy)Ru^{IV}=O]^{2+} + PPh_3 \xrightarrow{\text{rapid}}$$

$$[(trpy)(bpy)Ru\text{-}OPPh_3]^{2+} (A)$$

$$\text{slow} \downarrow + CH_3CN$$

$$[(trpy)(bpy)Ru^{II}\text{-}NCCH_3]^{2+} + O=PPh_3 \qquad (1)$$

The stoichiometry and product identification for above reaction were established from phosphine peak area analysis using ³¹P-NMR spectrophotometer and from P=O stretching frequency band area by FT-IR spectrophotometer. The intermediate (A) in the stepwise reaction was thoroughly studied by various spectroscopic techniques.

The UV-visible spectral changes in the oxidation of triphenylphosphine with [(trpy)(bpy)Ru^{IV}=O]²⁺ showed that an intermediate was rapidly appeared at 484 nm. The electronic characteristrics of the intermediate are typical of a great many polypyridyl complexes of Ru(II), especially those with oxygen-bound ligands, L, in the examples of complexes of the type [(bpy)₂(py)Ru^{II}(L)]²⁺ (*e.g.*: L=OH₂, λ_{max}=470 nm; L=OH⁻, λ_{max}=488 nm; L=OPPh₃, λ_{max}=479 nm; L=OS(CH₃)₂, λ_{max}=476 nm)[5-7] and [(trpy)(bpy)Ru^{II}-OH₂]²⁺, λ_{max}=476 nm.[8] This intermediate was slowly solvolyzed to give [(trpy)(bpy)Ru^{II}-NCCH₃]²⁺ (λ_{max}=456 nm). The rate of solvolysis of this intermediate was slower by more than 7 times than that of [(trpy)(bpy)Ru^{II}-OH₂]²⁺ by CH₃CN ($t_{1/2}$=15 min *vs.* 110 min).[9]

Shown in Figure 1 was the portion of ¹H-NMR spectral
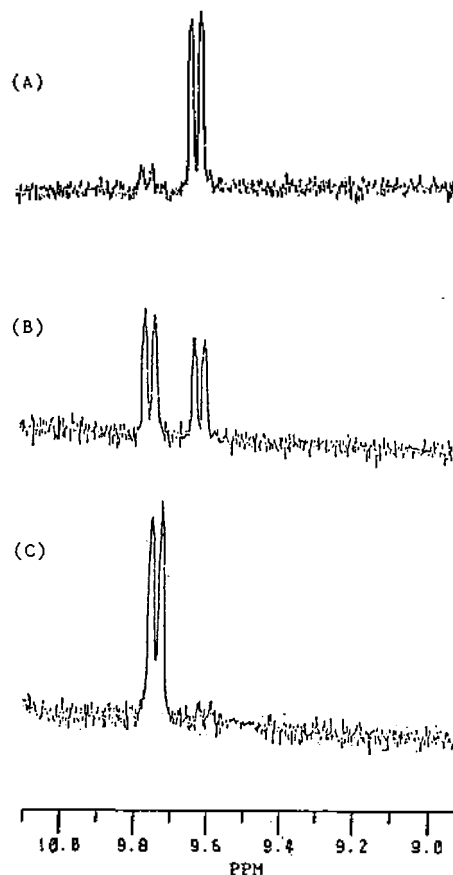
Figure 1. The portion of ¹H-NMR spectral changes of one of two 6-positioned protones in the bipyridine region for a reaction mixture containing PPh₃ (19 mM) and [(trpy)(bpy)Ru^{IV}=O]²⁻ (20 m) in 1 m*l* of CD₃CN at (A) as soon as mixing, (B) 4 h, and (C) 16 h.

changes in the bipyridine region obtained after allowing 5 mg of triphenylphosphine (19 mM) to react with 14 mg of [(trpy)(bpy)Ru(O)]²⁺ (20 mM) in 1 m*l* of CD₃CN. After mixing, the reactions occurred in a stepwise fashion *via* an intermediate appeared at 9.74 ppm followed by subsequent slower solvolysis product [(trpy)(bpy)Ru^{II}-NCCD₃]²⁺ at 9.60 ppm in the bipyridine region.

The one of 6′-proton of the bipyridine ring (primed notation refers to one of two 6 positioned protons of the pyridyl groups of the bipyridine ligand.) that is nearer to L in diamagnetic complexes of the type [(trpy)(bpy)Ru^{II}(L)]²⁺ exists out of ring current of aromatic terpyridine ligand as was seen from the molecular model[10] and the X-ray crystal structure of [(trpy)(bpy)Ru(OH₂)]²⁺.[11] Although we can not assign the structure of an intermediate only from this peak, the formation of the Ru(II) complex with different ligand environment will certainly be assumed. With the aid of UV-visible spectrum of the intermediate, the doublet of the 6′-proton in the bipyridine region at 9.74 ppm presumably indicates the presence of the O-bound triphenylphosphine oxide complex, [(trpy)(bpy)Ru^{II}-OPPh₃]²⁺.

Under the condition that PPh₃ is in slight excess against Ru(IV), ³¹P-NMR spectral changes were also investigated (Figure 2). As soon as they were mixed, an absorption band

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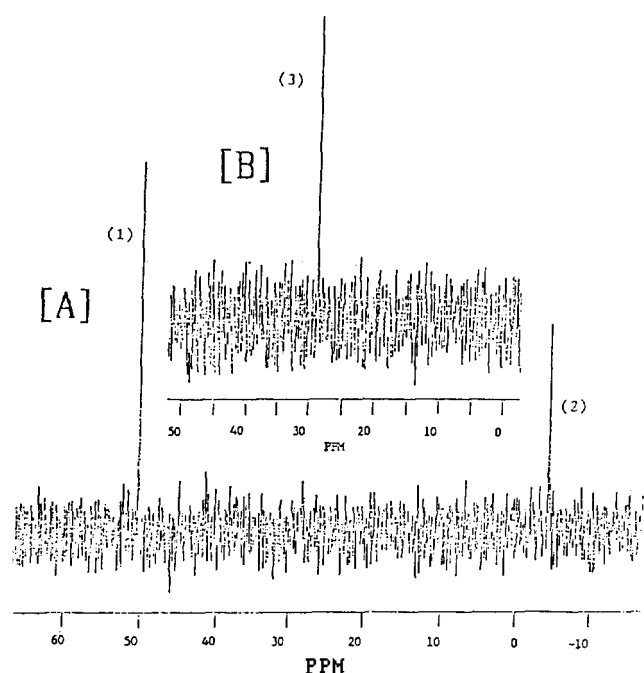
Figure 2. ^{31}P-NMR spectral changes in a reaction mixture of PPh$_3$ (2.8 mM) and [(trpy)(bpy)Ru^{IV}=O]$^{2+}$ (2.0 mM) in 10 m/ of CH$_3$CN referenced to external 85% H$_3$PO$_4$ at [A] as soon as mixing and [B] after the completion of the reaction. Here (1) indicates the intermediate, (2) PPh$_3$, and (3) O=PPh$_3$.

at ~4.50 ppm, triphenylphosphine, and additional absorption band at 49.5 ppm were seen in the ^{31}P-NMR spectra.[12] After 1 hr, the major absorption band slowly appeared at 27.4 ppm, triphenylphosphine oxide, by the expense of decrease of the 49.5 ppm absorption peak. After completion of the reaction, triphenylphosphine oxide was obtained as the sole product as evidenced by ^{1}H-NMR spectrophotometer and Gas Chromatography. The experiments were repeated with [(bpy)$_2$(py)Ru^{IV}(O)]$^{2+}$ (py is pyridine.) as oxidant. In this case an absorption band at 50.1 ppm was obtained in the ^{31}P-NMR spectral data.[9] The large downfield chemical shift of the intermediate against O=PPh$_3$ reflects the depletion of electron density on the phosphorous by the ruthenium metal.

In another experiment, FT-IR spectral change of an equimolar reaction mixture of triphenylphosphine and [(trpy)(bpy)Ru(O)]$^{2+}$ in CD$_3$CN was investigated. The P=O stretching frequency of triphenylphosphine oxide at 1195 cm^{-1} was normally shifted by *ca.* 42±6 cm^{-1} to a lower frequency when it coordinated to a metal *via* its oxygen atom[13] We found that "P=O" stretching band at 1161 cm^{-1} for [(trpy)(bpy)Ru^{II}-OPPh$_3$]$^{2+}$ indicates or shows more P=O double bond character.[14] For this diamagnetic d^6 complexes, there might be a drift of metal dπ electrons toward oxygen pπ orbitals. So this would probably tend to raise the force constant, K$_{P=O}$.

Attempts to isolate [(trpy)(bpy)Ru^{II}-(OPPh$_3$)]$^{2+}$ in pure stable form from the reaction did not yield analytically acceptable results probably due to the labile nature of the

OPPh$_3$ ligand bound to Ru(II). But the solid isolated by the reaction of [(trpy)(bpy)Ru^{II}-OH$_2$]$^{2+}$ with OPPh$_3$ did have spectral characteristics (IR, UV-visible, ^{1}H, and ^{31}P-NMR spectrophotometers) consistent with those expected for the metal phosphine oxide complex.

The results of these experiments point to the structure of the intermediate in the oxidation of PPh$_3$ by [(trpy)(bpy)Ru^{II}=O]$^{2+}$ in acetonitrile solution. The spectral characteristics are consistent with the triphenylphosphine oxide bound to the ruthenium metal complex. The kinetics of the formation of the intermediate in CH$_3$CN is in progress.

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